

The University of Chicago

DETERMINATIONS OF THE
DENSITY OF SOLUTIONS OF SALTS
IN LIQUID AMMONIA

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1935

By
ROBERT IVAN MARTENS

Private edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 58, 15 (1936)

1935

The University of Chicago

DETERMINATIONS OF THE DENSITY OF SOLUTIONS OF SALTS IN LIQUID AMMONIA

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1935

By
ROBERT IVAN MARTENS

Private edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 58, 15 (1936)



The Density of Solutions of Alkali Metal Halides in Liquid Ammonia

BY ROBERT I. MARTENS

Investigations of liquid ammonia solutions are often hampered by the lack of sufficient physical data. The density of solutions of the more common salts represents one type of measurement which has received little attention. Although the density of solutions of some of the alkali metals and saturated solutions of salts has been determined in a few instances, no systematic study of salt solutions has been made, with the exception of the work reported by Fitzgerald.¹ His measurements include salts which exhibit a high solubility in ammonia: ammonium bromide, cupric nitrate, silver iodide, silver nitrate, sodium nitrate and potassium iodide. They extend over a fairly long range of concentration but at a single temperature, -33.5° , the normal boiling point of the solvent.

In the present investigation the density of solutions of the chlorides, bromides and iodides of lithium, sodium and potassium in liquid ammonia is determined at temperatures ranging from -32 to -60° and over as wide a range of concentration as the solubility permits.

Apparatus and Procedure

Materials.—The ammonia used in the determinations was twice distilled from metallic sodium. The salts were of the best grade obtainable and were further purified by crystallization from distilled water solution. Before use, potassium iodide, potassium bromide and sodium chloride were fused, while all the other salts were heated above 100° in a high vacuum for several hours. To substantiate the purity, the halide content of each salt was determined gravimetrically, and found to deviate from the theoretical value by not more than 0.1% with the exception of lithium iodide. The latter salt was found to be 0.4% low in iodine content, probably due to hydrolysis during the removal of the last traces of water.

The Density Tube.—The essential portion of the apparatus employed in the density measurements is shown in Fig. 1. It consists of a small ammonia tank W connected to the density tube A which in turn is sealed through the top part of the glass ground joint K. The latter connects with a large Dewar tube, the internal dimensions of which are 40×4.5 cm. The density tube A, as far as the point P, has a volume of about 9 cc. The capillary stem extending for about 15 cm. above the bulb at the bottom has an inside diameter of 1.8 mm. and is graduated at regular intervals slightly greater than 1 mm. apart. The volume of this tube and stem was calibrated at several

points on the stem with mercury and also with liquid ammonia. A small glass tube H is sealed through the top part of the glass ground joint R with Picein cement. Through this tube there is sealed at U with Picein cement a Chromel wire heating coil which extends nearly to the bottom of the Dewar tube. This serves to keep the liquid ammonia in the Dewar tube boiling constantly. Copper-constantan thermocouple wires are sealed into tube F at Q and likewise extend to the bottom of the Dewar tube. This thermocouple was calibrated by observing the e. m. f. at the freezing point of chloroform and of mercury; a check determination was obtained by following the vapor pressure of pure ammonia from -30 to -60° . At -30° the change in the vapor pressure of ammonia per degree centigrade is almost 4 cm. The values so obtained, together with the ice point at 0° , were plotted and compared with the standard couple. M leads to a manometer, S to the vacuum pumps, and L to a thermostat regulator. The latter was designed to maintain a constant pressure of ammonia vapor above the liquid in the Dewar tube. Its operation was based on the method

previously described by Smith.² No difficulty was experienced in controlling the temperature in the Dewar tube, surrounding the density tube, to 0.1° , over a period of twelve to fifteen hours.

Procedure.—The density tube A, removed from the apparatus at P, is thoroughly cleaned and dried. A weighed amount of the salt is transferred quantitatively to the tube which is then sealed to the system at P and evacuated. With stopcock S closed, ammonia is condensed on the salt in A from tank W at a temperature of -80° . The valve to the ammonia tank is closed when a sufficient amount of the gas has condensed, so that upon warming the tube and its contents to the temperature of the measurements the level of the liquid will be in the capillary tube. When the pressure of the ammonia gas within the system has dropped to a constant value, the capillary tube is closed at P with a small flame. With the volume of all parts of the system known, the amount of ammonia left in the vapor phase in the connecting tubes is readily determined. The small ammonia tank may be weighed on a 1-kg. balance with an accuracy of 1 mg., thereby rendering

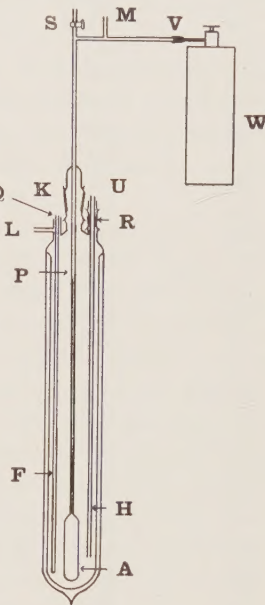


Fig. 1.

(1) Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912).

(2) Smith, *Ind. Eng. Chem.*, **16**, 22 (1924).

an accurate determination of the amount of ammonia condensed in A.

The density tube is then shaken to dissolve all of the salt. Finally it is placed in the Dewar tube through the joint K as shown in Fig. 1 and allowed to come to temperature

equilibrium with the ammonia bath. Not more than half an hour is required for the temperature of the bath and the height of the liquid in the capillary stem to assume constant values. After readings are taken, the system is allowed to come to equilibrium at a lower temperature.

TABLE I
EQUATIONS FOR DENSITY DATA

Series	Salt	Mole fraction salt	Equation	B	Temp. range, °C.	Max. % dev.
A ₁	LiCl	0.00111	-1.237	0.6423	-32.4 to -46.8	-0.05
A ₂	LiCl	.00168	-1.203	.6448	-32.2 to -34.8	— .01
B ₁	NaCl	.00244	-1.210	.6474	-41.1 to -57.9	— .01
B ₂	NaCl	.00381	-1.164	.6521	-40.8 to -51.5	— .05
B ₃	NaCl	.00458	-1.240	.6518	-33.2 to -50.5	— .03
B ₄	NaCl	.00546	-1.216	.6535	-35.2 to -49.6	— .01
B ₅	NaCl	.00704	-1.148	.6596	-32.1 to -39.7	— .02
C ₁	KCl	.00026	-1.285	.6388	-36.4 to -47.0	— .05
C ₂	KCl	.00043	-1.231	.6422	-32.2 to -46.5	— .01
D ₁	LiBr	.00246	-1.257	.6479	-32.5 to -49.5	— .03
D ₂	LiBr	.00381	-1.165	.6566	-32.3 to -45.0	— .02
E ₁	NaBr	.00128	-1.206	.6465	-47.8 to -58.6	— .01
E ₂	NaBr	.00334	-1.262	.6525	-33.8 to -52.2	— .02
E ₃	NaBr	.01392	-1.205	.6948	-40.2 to -57.0	— .01
E ₄	NaBr	.02220	-1.225	.7245	-33.3 to -45.6	— .01
F ₁	KBr	.01151	-1.164	.6935	-42.9 to -61.5	— .02
F ₂	KBr	.02702	-1.186	.7546	-32.3 to -40.7	— .01
F ₃	KBr	.04057	-1.280	.8056	-34.9 to -49.9	— .02
F ₄	KBr	.05299	-1.188	.8579	-32.3 to -47.1	— .02
G ₁	LiI	.00334	-1.214	.6581	-32.1 to -42.4	— .02
G ₂	LiI	.00441	-1.200	.6644	-32.2 to -40.2	— .02
G ₃	LiI	.00865	-1.238	.6830	-32.2 to -52.0	— .01
G ₄	LiI	.01372	-1.190	.7095	-32.2 to -47.4	— .01
G ₅	LiI	.01863	-1.212	.7319	-32.2 to -49.0	— .02
G ₆	LiI	.03151	-1.185	.7953	-32.1 to -45.6	— .02
G ₇	LiI	.03976	-1.158	.8354	-32.2 to -42.5	— .01
G ₈	LiI	.04205	-1.163	.8452	-32.4 to -44.1	— .03
H ₁	NaI	.00696	-1.183	.6800	-32.3 to -40.8	— .01
H ₂	NaI	.01888	-1.164	.7432	-33.6 to -47.5	— .04
H ₃	NaI	.03269	-1.217	.8133	-33.5 to -36.3	— .01
H ₄	NaI	.04274	-1.255	.8627	-32.4 to -58.0	— .03
H ₅	NaI	.05716	-1.167	.9382	-33.3 to -42.6	— .02
H ₆	NaI	.06320	-1.196	.9669	-32.3 to -47.4	— .02
H ₇	NaI	.07387	-1.175	1.0191	-32.1 to -36.1	— .01
I ₁	KI	.00174	-1.235	0.6509	-32.4 to -44.7	— .02
I ₂	KI	.00463	-1.294	.6655	-32.5 to -41.8	— .02
I ₃	KI	.01007	-1.245	.6979	-35.4 to -52.3	— .03
I ₄	KI	.01608	-1.235	.7324	-32.3 to -45.5	— .02
I ₅	KI	.02318	-1.272	.7700	-32.4 to -50.5	— .01
I ₆	KI	.02811	-1.272	.7958	-32.2 to -49.4	— .03
I ₇	KI	.03327	-1.280	.8232	-32.4 to -45.9	— .03
I ₈	KI	.04137	-1.197	.8720	-32.2 to -40.9	— .02
I ₉	KI	.05386	-1.228	.9346	-32.1 to -42.8	— .01
I ₁₀	KI	.06044	-1.273	.9662	-32.3 to -48.3	— .03
I ₁₁	KI	.07138	-1.264	1.0216	-32.5 to -52.0	— .01
I ₁₂	KI	.09023	-1.294	1.1127	-32.4 to -52.7	— .02
I ₁₃	KI	.09789	-1.286	1.1476	-32.2 to -54.3	— .02
I ₁₄	KI	.1055	-1.270	1.1826	-32.3 to -49.3	— .01
I ₁₅	KI	.1146	-1.300	1.2239	-32.2 to -58.1	— .01
I ₁₆	KI	.1292	-1.274	1.2871	-32.3 to -51.9	— .01
I ₁₇	KI	.1456	-1.273	1.3551	-32.2 to -48.5	— .01
I ₁₈	KI	.1513	-1.345	1.3750	-32.3 to -54.6	— .01
I ₁₉	KI	.1585	-1.325	1.4028	-32.1 to -58.0	— .02

Thus, it is readily possible to obtain a series of readings for a given salt at a single concentration over a considerable range of temperature.

Results

The results of the density measurements are recorded in the preceding table. Since the density was found to be a linear function of the temperature in each case, the data are represented by the equation

$$d_4 = At + B$$

where d_4 is the density, relative to water at 4°, t the temperature on the centigrade scale, and A and B are constants. The last column of the table gives the maximum percentage deviation of any point from the linear expression.

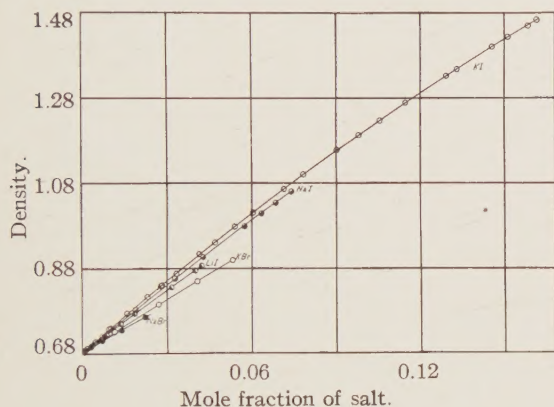


Fig. 2.—Densities of salt solutions at -34° .

In Fig. 2 the density of the solutions is plotted as a function of the concentration at -34° . The values were obtained from the density-temperature plots represented by the equations of Table I. Lithium bromide and the chlorides of lithium, sodium and potassium are not shown in this figure due to their extremely low solubilities. The density of pure ammonia, shown in the figure at zero concentration of solute, was taken as 0.6826 from the tables of Cragoe and Harper.³

It will be observed from these curves that those for the iodides have a greater slope than those of the bromides; and in turn the curves for the bromides are steeper than those for the chlorides (chlorides not shown in this figure). In addition, within each of these groups the curve for the potassium salt shows the greatest slope and that for the lithium salt the least slope. It appears that at the lower concentrations the density is a linear function of the mole fraction of dissolved salt. In the case of some of the slightly soluble salts men-

tioned above measurements were made at only two concentrations; nevertheless a linear extrapolation to zero concentration on an enlarged plot similar to that of Fig. 2 was found to intersect the axis at a point corresponding to the density of pure ammonia.

The results of Fitzgerald's determinations of the density of potassium iodide at -33.5° are in excellent agreement with the present data. He carried out six determinations in the more dilute solutions, and in no case does a point calculated from his data show a departure greater than 0.1% from the curve through points representing the present determinations at the same temperature.

A consideration of all of the possible errors involved in the procedure outlined above allows for an estimation of a net error not to exceed 0.1%. It is very probable that most of the values are well within this estimate.

It has been discovered by Masson⁴ as an empirical rule that for a great many water solutions a linear relationship exists, even in very concentrated solutions, between the apparent molal volume of the solute and the square root of the concentration expressed in moles per liter of solution. In order to find if this relationship could be extended to liquid ammonia solutions, such a plot was made for the potassium iodide solutions at -34° (Fig. 3). It will be observed that the values agree fairly well with this linear relationship.

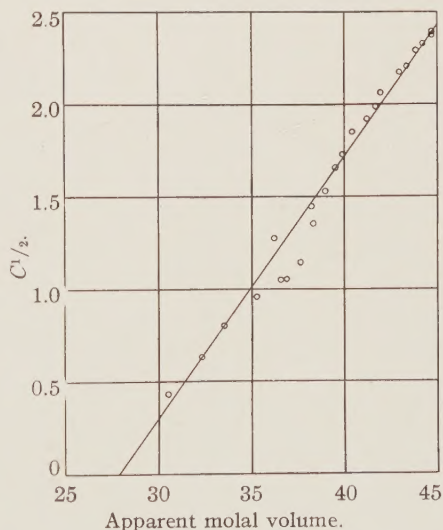


Fig. 3.—The apparent molal volume of ammonia solutions.

Summary

The density of solutions of the chlorides, brom-

(3) Cragoe and Harper, *Bur. Standards, Sci. Papers*, **420**, 313 (1921).

(4) Masson, *Phil. Mag.*, **8**, 218 (1929).

ides and iodides of lithium, sodium and potassium has been determined over a range of concentration and of temperature. A method for carrying out these measurements is described.

